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# **PCT**

# WORLD INTELLECTUAL PROPERTY ORGANIZATION International Bureau



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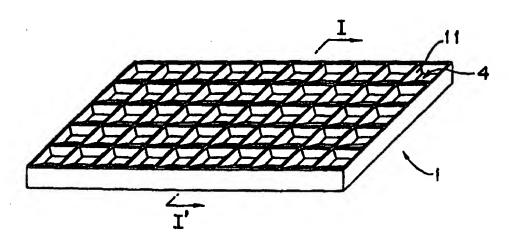
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(54) Title: CUSHIONING ADHESIVE SHEET AND CUSHIONING STRUCTURE



#### (57) Abstract

A cushioning adhesive sheet for which the cushioning ability is not likely to be deteriorated with time, by applying an airtight space having a comparatively large volume on an adherend and maintaining the airtight space stably with time. The cushioning adhesive sheet comprises: i) a base part; and ii) a convex part consisting of a crosslinked adhesive polymer and having an adhesive surface, which is provided on at least one major surface of the base part so as to enclose a plurality of concave parts having a geometric shape; wherein a volume of the concave part is 0.8 to 600 mm³, a modulus G of the convex part measured according to a dynamic viscoelasticity measuring method at a frequency of 1 rad/second under shear mode at 25 °C is within a range of 5 x 105 to 4 x 106 dynes/cm², and a decrease of log10G within a range of 25 to 125 °C is less than 1.0.

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#### CUSHIONING ADHESIVE SHEET AND CUSHIONING STRUCTURE

#### **BACKGROUND OF THE INVENTION**

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#### Technical field

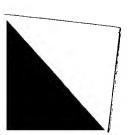
The present invention relates to an adhesive sheet. More particularly, the present invention relates to a cushioning adhesive sheet.

#### 10 <u>Description of the Related Art</u>

Adhesive sheets having an adhesive layer with a (regular) concave-convex pattern are disclosed in several references.

For example, in Japanese Laid-Open Utility Model Publication No. B20043, there is disclosed an adhesive sheet (100), as shown in Fig. 5, having a surface sheet (101) and an adhesive layer comprising a plurality of independent small convex parts (102). The height of the convex part (102) is comparatively small, for example, about 3 to 50 µm. As is apparent from Fig. 5, no airtight space is formed between the adherend and adhesive layer at the state where it is adhered on the adherend. In addition, it does not intend to maintain such an airtight space. It is intended that the adhesive layer is adhered easily without involving air between the adherend and the adhesive layer and, after completion of application, the small convex part (102) flows and becomes flat and the adhesive area increases and the adhesive force improves.

In Japanese Laid-Open Patent Publication No. 3-1811578 (corresponding to U.S. Patent No. 5,141,790), there is disclosed a positionable adhesive tape (200), as shown in Fig. 6, having a plurality of convex parts (203) on an adhesive layer (201), said convex parts containing a plurality of particle groups (202) at the tip thereof. In this adhesive tape, it is suggested that good positionability can be obtained by adjusting the distance between convex parts (203) to 0.1 to 0.5 mm, because an adhesive surface (204) of the concave part present between convex parts does not contact the adherend. Similar to the above adhesive sheet, however, it is intended that the convex part (203) flows and becomes flat after the completion of



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positioning. Accordingly, it is impossible to form an airtight space between the adherend and the adhesive layer and impossible to maintain the airtight space while using at the state where the adhesive tape is adhered on the adherend.

In Japanese Laid-Open Utility Model Publication No. 170848, there is suggested to provide a concave-convex pattern having a regular shape such as a network pattern for the purpose of increasing the adhesive area onto a non-flat adherend surface such as wall paper, etc. However, there is no description about forming an airtight space due to the concave-convex pattern having a network pattern.

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In Japanese Laid-Open Patent Publication No. 7-126582, there is disclosed an adhesive tape comprising an substrate and an adhesive layer having a concave-convex pattern with a regular shape and an arrangement of 1 mm or less in pitch on the surface, the adhesive layer being provided on the substrate. This concave-convex pattern has an extremely fine structure consisting of a convex part having a height of 20 µm or less and an concave part having a depth which is 10 to 90% of the height of the convex part. The adhesive consists of a n-butyl acrylate-acrylic acid copolymer and a polyisocyanate compound, the amount of the isocyanate compound being 1 g based on 100 g of the copolymer. Since a concave-convex pattern of the adhesive layer of this adhesive tape is not deformed even after it was adhered on the adherend, the pattern can be visually recognized as literature, figure, symbol, etc. through the substrate. However, regarding such a concave-convex pattern, an extremely small airtight space can be formed, which results in no cushioning ability.

In W095/11945, there is disclosed an article comprising an adhesive layer having a microstructured surface which can form a space having a volume of about 1 x 10<sup>-3</sup> mm<sup>3</sup> between the article and the adherend. This adhesive layer is formed by UV polymerizing a monomer mixture comprising 90 parts of isooctyl acrylate, 10 parts of acrylic acid, and a comparatively small amount of a crosslinking agent (0.1 parts of 1,6-hexanediol diacrylate). In W095/11655, there is disclosed a tape comprising an adhesive layer having the same microstructured surface as that described above.

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These adhesive products having the microstructured surface have no cushioning ability because an extremely small airtight space is formed.

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On the other hand, there have widely been known sheet materials made of a polymer material in which a plurality (i.e. many) airtight spaces having a comparatively large volume and concave-convex patterns are provided on almost the entire surface. The sheet materials can absorb, subside or release an external action such as impact, vibration (including sound), heat, etc. These materials are applied as cushioning materials (including cushioning materials and shock-absorbing materials), vibration-deadening materials (vibration-damping materials), soundproofing materials (sound-absorbing materials, sound insulating materials) or warming materials (insulating materials). In addition, they can have any one of these functions or two or more functions.

References disclosing sheets which enclose an airtight space are known. For example, in Japanese Laid-Open Patent Publication No. 63-53024, there is disclosed a insulating sheet for applying to glass, comprising an insulating layer consisting of a cushioning material which encloses a plurality of independent partitions and a self-adhesive plastic film layer provided on at least one surface thereof. In this sheet, the insulating layer is provided by laminating a first concave-convex film and a second flat film, and the closed partition in the sheet corresponds to the concave part. The sheet is applied on an object such as an window through a self-adhesive film.

A soundproofing sheet of Japanese Laid-Open Patent Publication No. 3-43241 teaches that energy passing through it is subsided and soundproofing performance is improved by laminating the first plate material superior in soundproofing properties having a concave-convex pattern on the whole surface thereof and the second plate material having excellent soundproofing properties, and by forming a hollow part between both materials.

Regarding a warm sheet of Japanese Laid-Open Utility Model Publication No. 56-176830, a plurality of independent projecting chambers are formed close to each other on an embossed film and the other flat film is laminated/adhered so as to close an opening part of this projecting chamber, and a plurality of independent hollow chambers, each of which has a volume of about 14 to 7,000 mm<sup>3</sup>, is formed on the whole surface, thereby exhibiting an excellent insulating effect.

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In Japanese Laid-Open Utility Model Publication No. 6088731, there is disclosed a solid-patterned decorative sheet of which the solid pattern can be visually recognized, which is applied on glass through an adhesive. This decorative sheet has a surface part comprising a pressed part at which the sheet completely adheres to the underlaid colored sheet and a figure thereon can be seen clearly and a non-pressed part at which the sheet does not adhere and a space is present, and a flat back surface part on which the pressed part is pressed, thereby, it has a sealed space in the sheet so that the concave-convex pattern is not easily broken by an external pressure.

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These articles such as insulating sheets are not those for forming an airtight space between the sheet and the adherend having an effective size. In addition, additional adhesive means are required for adhering to the adherend.

Also known are references disclosing a concave-convex part which contacts an adherend. The soundproofing insulator of Japanese Laid-Open Patent Publication No. 3-213334 is obtained by laminating glass wool as a porous material, a film of which one surface is applied a polyethylene resin (EVAPG) added an ethylene vinyl acetate copolymer as a thermoplastic synthetic film, and a skin material of a soft polyurethane foam. The insulator is easily processed into a complicated concave-convex shaped product, such as dashpanel, and is superior in cushioning properties.

In the cushioning material of Japanese Laid-Open Patent Publication No. 4-351538 and a soundproofing floor using the same, a concave-convex synthetic resin sheet is laminated/adhered on the back surface of a foamed polyurethane resin sheet having a high extent of foaming to form a cushioning material, which is adhered appropriately on a floor base plate through a nonwoven fabric to improve a soundproofing effect. This floor covering material is deposited on use so that the convex part is brought into contact with the adherend floor surface.

The cushioning sheet of Japanese Laid-Open Utility Model Publication No. 4-79105 has a plurality of projections for adhering to a backing, and a plurality of projections for supporting the sheet itself on an object. Regarding this sheet, an adhesive surface of the projection for adhering the backing is flat and, therefore, it can be adhered strongly on the backing. In addition, the flat surface and a tip part of the projection for supporting the sheet are deposited so that they are not present in the same region, when they are viewed from a section in the thickness direction of

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the cushioning sheet. Therefore, the impact force applied to the backing is not transmitted linearly to the object. The projection for supporting is not adhered on the surface of the object and is used so that no airtight space is formed between the object and the sheet.

The action (e.g. sound absorption, insulation, etc.) of these materials such as insulator are mainly derived from the constitution material and/or shape of the projection, and are not obtained by using an airtight space.

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Other references describe articles capable of self-adhering to an adherend. In Japanese Laid-Open Utility Model Publication No. 440741, there is disclosed an adhesive material obtained by forming a concave-convex pattern on one major surface of elastic substrate such as foamed polyethylene, and applying an pressure-sensitive adhesive on the concave-convex surface. This adhesive material requires no additional adhesive means and can be fixed by adhering on the surface of an object by an adhesive force of 100 to 500 g/cm<sup>2</sup>. Therefore, it is suitable as a protective cover of the object.

A vibration-deadening layer provided in the magnetic optical disc of Japanese Laid-Open Utility Model Publication No. 4-126369 consists of an adhesive layer having a thickness of at least about 25.4 μm, said adhesive layer being made of an UV crosslinked isooctyl acrylate-acrylic acid copolymer, and a polyester film having a thickness of at least about 102 μm. This vibration-deadening layer inhibits vibration of the disc of at a frequency of at least 850 Hz.

The adhesive material and vibration-deadening layers are composed of an adhesive polymer material and have self-adhesiveness, but they are not for forming an airtight space between them and the applied adherend.

Several references disclose articles capable of forming an airtight space between themselves and the adherend. In Japanese Laid-Open Utility Model Publication No. 462520, there is disclosed an information recording optical medium obtained by laminating two recording mediums to each other with a double surface adhesive film. The cushioning effect of the adhesive due to a concave-convex pattern which is provided on at least one adhesive layer of the double surface adhesive film, can eliminate the deformation due to the warpage of the medium, effectively, even if a thermal action is applied externally. However, the thickness of

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the adhesive layer is preferably about 10 to 50  $\mu$ m and the volume of the airtight space to be formed by the adhesive layer is comparatively small, which results in low cushioning ability.

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The air-enclosed cushioning material of Japanese Laid Open Utility Model Publication No. 5-70933, as shown in Fig. 7, consists of an adhesive film (302) and a non-adhesive film (307), both films being laminated to each other, and a second flat synthetic resin film (304) is laminated on a first synthetic resin film (301) having a plurality of concave parts at the adhesive film side through an adhesive film (305) so as to cover an opening part of a concave part (303), thereby forming an independent air chamber (306).

Accordingly, the cushioning material can be easily assembled at the site on use without heating for laminating synthetic resin films, and is not bulky at the time of preserving and transporting. This adhesive film is made by mixing an adhesive with a thermoplastic resin such as polyacryls, etc. However, there is not disclosed effective means for stably maintaining the volume and shape of the airtight space (air chamber) without using a non-adhesive film (307) corresponding to the concave-convex pattern of the adhesive film (e.g. crosslinking of adhesive film, its modulus).

Summing up the above, in an article containing an adhesive, such as conventional adhesive sheet, it is not intended to form an airtight space having a comparatively large volume, which can exhibit the effect such as cushioning, insulation, etc.

In addition, in the article having an airtight space having a comparatively large volume, it is necessary that the article already enclose the airtight space before it is applied on the adherend, and/or additional adhesive means are required at the time it is applied on the adherend. When the article itself encloses the airtight space, the airtight space is sometimes deflated or broken during transporting or preserving before use, which results in deterioration of performance such as cushioning ability, etc. On the other hand, when additional adhesive means are required at the time of applying, the processes on use are increased and, therefore, it is inconvenient.

On the other hand, Japanese Laid-Open Utility Model Publication No. 5-70933 discloses a cushioning material which can form an airtight space having a comparatively large size between it and an applied adherend (in this case, the second

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flat synthetic resin film (304) corresponds to it). However, a non-adhesive film processed to follow the shape of the space (concave-convex pattern) is required in order to stably maintain the airtight space.

Furthermore, it is not easy to laminate a non-adhesive film having a comparatively strong nerve and an adhesive film having a comparatively weak nerve to each other with good adhesion and to form a concave-convex shape. Therefore, a freedom for design of the size of the airtight space becomes poor.

#### SUMMARY OF THE INVENTION

The present invention solves the above conventional problems. An object of the present invention is to provide a cushioning adhesive sheet which forms an airtight space of comparatively large volume on an adherend on the place by laminating it, and maintains the airtight space stably with time so that the cushioning ability does not deteriorated with time.

More particularly, the present invention provides a cushioning adhesive sheet, comprising:

(i) a base part; and

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(ii) a convex part comprising a crosslinked adhesive polymer and having an adhesive surface which is provided on at least one major surface of the base part so as to enclose a plurality of concave parts having a geometric shape;

wherein a volume of the concave part is 0.8 to 600 mm<sup>3</sup>, a modulus G of the convex part measured according to a dynamic viscoelasticity measuring method at a frequency of 1 rad/second under shear mode at 25°C is within a range of 5 x  $10^5$  to 4 x  $10^6$  dynes/cm<sup>2</sup>, and a decrease of  $\log_{10}$  G within a range of 25 to 125°C is less than 1.0.

A cushioning structure having an airtight space consisting of an adherend surface and an inner surface of the concave part is provided by adhering the above cushioning adhesive sheet on a surface of the adherend.

#### 30 BRIEF DESCRIPTION OF THE DRAWINGS

The invention will be more fully appreciated with respect to the following drawings in which:

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Fig. 1(a) is a perspective view illustrating one embodiment of the cushioning adhesive sheet of the present invention, and Fig. 1(b) is a sectional view taken in the line I-I' of Fig. 1(a).

- Fig. 2(a) and Fig. 2(b) are sectional views illustrating one embodiment of the cushioning structure of the present invention, respectively.
  - Fig. 3(a) is a sectional view illustrating one embodiment of the cushioning structure of the present invention, and Fig. 3(b) is a penetrative top view of Fig. 3(a).
  - Fig. 4(a) and Fig. 4(b) are schematic sectional views illustrating the process for producing the cushioning adhesive sheet of the present invention.
  - Fig. 5 is a perspective view illustrating one embodiment of a conventional adhesive sheet.
  - Fig. 6 is a sectional view illustrating one embodiment of a conventional adhesive sheet.
- Fig. 7 is a sectional view illustrating one embodiment of a conventional cushioning sheet.

#### DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

Hereinaster, the present invention will be explained in detail with reference to Figs. 1(a), 1(b), 2(a) and 2(b).

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#### **Base Part**

Base part (10) may be composed of the same material as that of the convex part (11) containing a crosslinked adhesive polymer and formed integrally with the convex part (11). The base part (10) may also be composed of a material which is different from that of the convex part (11), i.e. material (e.g. plastic film, metal foil, etc.) capable of fixing the convex part (11) containing the crosslinked adhesive polymer, and the base part serves as a substrate of the convex part (11). However, it is suitable to form the convex part (11) integrally with the base part (10) in view of the fact that the cushioning adhesive sheet can be easily produced and a comparatively strong impact force can be released by enhancing a fixing force at the interface between the convex part (11) and base part (10).

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The thickness of the base part (10) is generally 0.05 to 3 mm, preferably 0.1 to 1 mm, more preferably 0.2 to 0.7 mm. When the thickness of the base part is less than 0.05 mm, the maintaining performance of the airtight space (41) is likely to be deteriorated. On the other hand, when it exceeds 3 mm, the cushioning adhesive sheet becomes bulky, which results in deterioration of handling and appearance after application. The cushioning adhesive sheet of the present invention is superior in cushioning ability even if it is comparatively thin, because the airtight space (41) has high airtightness and the convex part (11) has a predetermined modulus.

In addition, when it is preferred that the plane major surface (5) of the base part (10) on which the convex part is not provided has no adhesiveness, a non-adhesive flexible substrate (6) can be laminated on the plane major surface (5) on which the convex part is not provided.

#### Convex Part

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The convex part (11) can take any shape unless the performance for maintaining the airtight space (41) is deteriorated. Preferably, the sectional shape thereof may be generally square, rectangular and trapezoidal, and a wall-like shape enclosing the concave part (4). The shape has an adhesive surface (12) with a sufficient area and is superior in processability.

The sectional shape of the convex part (11) is preferably rectangular having a width of 0.1 to 5 mm, particularly 0.5 to 3 mm. Otherwise, the convex part (11) is a trapezoid having an upside of 0.1 to 5 mm, particularly 0.2 to 3 mm, and a base of 0.2 to 10 mm, particularly 0.5 to 7 mm.

As shown in Fig. 1, the convex part (11) can be provided on an end edge of the base part (10) to form an airtight space on the whole surface when applying on an adherend. Otherwise, the convex part is not formed on an end edge of the base part (10) to remain a handgrip which makes it easy to peel off.

#### Modulus of the Convex Part

The modulus G of the convex part (11) when measured at a frequency of 1 rad/second under shear mode according to a dynamic viscoelasticity measuring method is  $5 \times 10^5$  to  $4 \times 10^6$  dynes/cm<sup>2</sup> at  $25^{\circ}$ C, preferably  $6 \times 10^5$  to  $2 \times 10^6$ 

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dynes/cm<sup>2</sup>, more preferably  $6.1 \times 10^5$  to  $1.5 \times 10^6$  dynes/cm<sup>2</sup>. In addition, a decrease of  $\log_{10}G$  within a range of 25 to  $125^{\circ}C$  is less than 1.0, preferably less than 0.5, more preferably less than 0.4.

Thereby, it becomes possible to maintain the volume and shape of the airtight space (41) with time, each space having a predetermined volume, when the cushioning adhesive sheet (1) is adhered on the adherend surface (31) to form a plurality of independent airtight spaces (41) where no external force is applied.

When the modulus G is less than  $5 \times 10^5$  dynes/cm<sup>2</sup>, the convex part (11) plastically flows with time after the cushioning adhesive sheet was adhered on the adherend surface (31), thereby it becomes impossible to form the airtight space (41). On the contrary, when the modulus G exceeds  $4 \times 10^6$  dynes/cm<sup>2</sup>, adhesiveness of the convex part (11) is deteriorated, and airtightness at the interface between the cushioning adhesive sheet (1) and adherend surface (31) is not obtained.

When the cushioning adhesive sheet (1) constitutes a cushioning structure, the modulus G of the convex part (11) at 25°C is preferably within a range of 6 x  $10^5$  to  $2 \times 10^6$  dynes/cm<sup>2</sup>. When it is not within this range, the remarkable improvement of the cushioning performance can not be expected.

On the other hand, when the decrease of log<sub>10</sub>G within a range of 25 to 125°C is larger than 1.0, that is, when a variation in log<sub>10</sub>G within this temperature range is smaller than -1.0, the convex part (11) plastically flows with time in the adhered cushioning adhesive sheet, thereby it becomes impossible to maintain the airtight space (41). When the log<sub>10</sub>G does not decrease at all or increase, such a plastic flow does not arise. However, when the modulus (i.e. log<sub>10</sub>G) of the convex part (11) increases, the degree of crosslinking of the adhesive polymer is insufficient at the time of forming the cushioning adhesive sheet, and the crosslinking may proceed with time and deterioration of the adhesive force may be caused. Accordingly, an increase in log<sub>10</sub>G is preferably +1.0 or less.

#### Concave Part

The concave part (4) forms a space enclosed by the surface of the base part and side of the convex part. Each concave part has a volume within a range of 0.8 to 600 mm<sup>3</sup>, preferably 0.9 to 150 mm<sup>3</sup>, more preferably 1.0 to 10 mm<sup>3</sup>. When the

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volume of the concave part is smaller than 1 mm<sup>3</sup>, the cushioning ability of the cushioning adhesive sheet is deteriorated. On the contrary, when it exceeds 600 mm<sup>3</sup>, the concave part (4) plastically flows with time and, at the same time, the cushioning action is also deteriorated.

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#### Arrangement of the Concave Part

Preferably, the concave part (4) is uniformly arranged on the almost all of the surface of the major surface (2) of the base part (10). Thereby, the airtight space-maintaining performance of the concave part (4) is enhanced. The concave part (4) can be regularly arranged, for example, in a lattice pattern or a cross pattern (checkered pattern). The number of concave parts (4) per unit area is generally 1 to  $50/\text{cm}^2$ , preferably 2 to  $25/\text{cm}^2$ . When the number of concave parts (4) is smaller than  $2/\text{cm}^2$ , the cushioning ability is likely to be deteriorated. On the contrary, when it exceeds  $25/\text{cm}^2$ , the cushioning ability is likely to be deteriorated because the volume of the concave part (4) becomes small.

The depth of the concave part (4), that is, the height of the convex part (11) is generally 0.5 to 10 mm, preferably 0.7 to 2 mm. When this depth is smaller than 0.5 mm, no effective cushioning action is likely to be obtained. On the other hand, when it exceeds 10 mm, the airtight space-maintaining performance is likely to be deteriorated.

The concave part (4) can take various shapes. Examples thereof include geometric solids such as cylinder, prism, pyramid, cone, truncated cone, near-sphere, near-ellipsoid, etc. The concave part (4) can also take a composite shape of one or more sorts selected from the group consisting of these shapes.

In addition, when it is applied on a transparent adherend or it is a cushioning adhesive sheet having a transparent base part, a groups of spaces consisting of a plurality of concave parts (4) is visually recognized as a sort of a solid pattern by an observer. Accordingly, the above space groups can take any form such as geometric arrangement pattern, literature, numeral, figure, indication of symbol, etc. so as to impart a design unless the effect of the present invention is deteriorated.

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#### Adhesive Polymer

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The convex part (11) comprising the crosslinked adhesive polymer adheres firmly on the adherend surface (31) and seals air of a predetermined volume in the interior and maintains the airtight space (41). Air in the interior of the airtight space (41) may leak from an adhesive interface between (i) the convex part (11) and adherend surface (31), or may leak through (ii) the convex part (11).

The crosslinked adhesive polymer is superior in adhesiveness, and improves the shape retention of the convex part (11) and barrier properties (impervious properties) of air, i.e. improves airtightness. In addition, the storage modulus controlled within a predetermined range and its decrease proportion imparts a suitable cohesive force to the convex part (11) and enhances the barrier properties thereof.

In the preferred embodiment, the crosslinked adhesive polymer is a crosslinked acrylic polymer formed by polymerizing a monomer component substantially comprising alkyl (meth)acrylates, ethylenically unsaturated acids and a crosslinking agent monomer having two or more (meth)acryl groups in the molecule. The crosslinked acrylic polymer is particularly superior in airtightness. Such an airtightness is particularly enhanced when the amount of the above crosslinking agent monomer is within a range of 0.5 to 5% by weight, based on the total amount of the monomer component.

When the amount is less than 0.5% by weight, the air barrier properties and shape retention are liable to be deteriorated. On the other hand, when it exceeds 5% by weight, adhesiveness is liable to be deteriorated. From such a point of view, a particularly preferred amount of the crosslinking agent monomer is within a range of 0.7 to 2% by weight.

As the alkyl (meth)acrylate, isooctyl acrylate is preferred. Because isooctyl acrylate imparts adhesiveness to the adhesive surface (12) of the convex part (11), effectively, and it makes easy the applying operation of the cushioning adhesive sheet. As the other alkyl (meth)acrylate, there can be used one or more sorts selected from alkyl acrylates or methacrylates, of which alkyl includes methyl, ethyl, isopropyl, butyl, isobutyl, isooctyl, 2-methylbutyl, 2-ethylhexyl, lauryl, stearyl, cyclohexyl, isobornyl, 2-hydroxyethyl, 2-hydroxypropyl, 3-chloro-2-hydroxypropyl.

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hydroxyethyl, methoxyethyl, ethoxyethyl, dimethylaminoethyl, diethylaminoethyl and glycidyl.

As the ethylenically unsaturated acid, (meth)acrylic acid is preferred. The (meth)acrylic acid effectively enhances the cohesive force of the adhesive polymer, and improves the shape retention of the convex part (11), thereby airtightness of the airtight space is enhanced, effectively. As the other ethylenically unsaturated acid, there can be used one or more sorts selected from  $\beta$ -hydroxyethyl carboxylic acid, itaconic acid, maleic acid and fumaric acid.

The formulation proportion of the alkyl (meth)acrylate (A) to ethylenically unsaturated acid (E) is selected so that the modulus of the convex part (11) becomes a value within a predetermined range, preferably within a range of 80:20 to 99:1 (A:E).

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In addition, as the crosslinking agent monomer having two or more (meth)acryl groups in the molecule, 1,6-hexanediol diacrylate is preferred. The 1,6-hexanediol diacrylate effectively enhances crosslink density of the adhesive polymer and improves adhesiveness, air barrier properties and shape retention with good balance.

The crosslinked adhesive polymer can be obtained by polymerizing a monomer component containing the above components as the starting material by using heat or radiation (e.g. ultraviolet ray, electron beam, etc.). For example, as described hereinafter, the monomer component is polymerized or crosslinked while contacting with a mold having a predetermined geometric structure to form a cushioning adhesive sheet (1). In this case, a preliminary component which contains a monomer component but does not contain a crosslinking agent monomer is partially polymerized, previously, and a mixture of the viscosity-adjusted partially polymerized syrup and the crosslinking agent monomer can be polymerized and crosslinked while contacting with a mold. In this case, the viscosity of the syrup is generally 100 to 100,000 cps.

In addition to the acrylic polymers, polyisoprene (a natural rubber), styrenbutadiene rubber, butyl rubber, nitrile rubber, silicone rubber, neoprene, polyisobutylene, polyvinyl ethers such as polyvinyl butyl ether, polyurethane, polyvinyl acetate, ethylene-vinyl acetate copolymer, poly-alpha-olefin and the like

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may be used as the adhesive polymer. The adhesive polymer may be used alone or in combination thereof.

As a crosslinking agent for the acrylic polymer, an isocyanate compound, an epoxy compound, melamine compound and the like may be used.

In another embodiment of the present invention, the adhesive sheet which is comprised of the adhesive polymer and the unreacted crosslinking agent is prepared and adhered to the adherend, thereafter the crosslinking reaction is conducted.

A curable resin may be employed together with the adhesive polymer unless it does not fail the technical effects of the present invention.

A thermoplastic resin which is non-tacky at ambient temperature may be employed together with the adhesive polymer unless it does not fail the technical effects of the present invention. If the convex part is composed of the adhesive polymer and the thermoplastic resin, and do not have sufficient adhesiveness, the convex part may be heated and tackified in order to adhere the adherend.

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#### Peel Strength of Cushioning Adhesive Sheet

The peel strength measured at 25°C when the cushioning adhesive sheet (1) is peeled off from the adherend surface (31) is preferably within a range of 20 to 2,500 g/25 mm, particularly within a range of 350 to 2,000 g/25 mm. When the peel strength is less than 20 g/25 mm, airtightness of the space (41) is likely to be deteriorated with time when it is applied on the vertical surface of the adherend. To the contrary, when it exceeds 2,500 g/25 mm, it becomes difficult to peel off the cushioning adhesive sheet (1) immediately after applying. It also becomes difficult to position for applying, which results in deterioration of operating properties.

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In addition, it is advantageous that the cushioning adhesive sheet which was once used can be used again by applying on another adherend. That is, the cushioning material comprising an adhesive surface (12) having re-peelablity, which can be used repeatedly, is useful in view of resources saving. From such a point of view, particularly preferred peel strength is 50 to 1,000 g/25 mm.

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#### **Cushioning Adhesive Sheet**

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The present cushioning adhesive sheet has a base part and a plurality of convex parts provided on the major surface of the base part so as to enclose a plurality of concave parts, said convex parts containing a crosslinked adhesive polymer, and a polymer of the adhesive polymer of the convex part being crosslinked and the convex part having a predetermined modulus. These facts make it possible to form an airtight space at the position on use only by applying the sheet on the adherend without requiring any adhesion means. In addition, they prevent a plastic deformation (natural flow) of the convex part as well as deformation and disappearance of the airtight space due to an external force, thereby, the volume and shape of the airtight space is stably maintained.

The concave part is designed so that the airtight space consisting of the concave part and adherend surface having a predetermined volume at the part where it is adhered. The fact exhibits a cushioning action, that is, it releases an impact force applied from the plane major surface of the base part on which no convex part is provided, before the impact transfers to the adherend.

The cushioning adhesive sheet (1) of the present invention is used as follows. The cushioning adhesive sheet (1) is disposed so that the adhesive surface (12) of the convex part (11) contacts with the adherend surface (31), and the cushioning adhesive sheet is softly pressed with hands, press roller, etc. from the side of the plane major surface (5) of the base part (10) on which no convex part is provided to adhere the adhesive surface (12) on the adherend surface (31). The convex part (11) contains an adhesive polymer and, therefore, it can adhere on the adherend surface of the cushioning adhesive sheet (1) by the same light press operation as that of a normal pressure-sensitive adhesive sheet. The adhered cushioning adhesive sheet (1) forms a plurality of independent airtight spaces (41) which is enclosed between the concave part (4) and adherend surface (31).

The facts that the modulus (measured value G) of the convex part (11) at 25°C is not less than 5 x 10<sup>5</sup> dynes/cm<sup>2</sup>, that the decrease of log<sub>10</sub>G within a range of 25 to 125°C is less than 1.0 and that the airtight space (41) is retained so as not to be broken by a constant pneumatic pressure, cooperate and maintain the shape and volume of the airtight space (41). The procedure for pressing can be carried out

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under the pressure by which the airtight space (41) is not broken, e.g. 10 kPa or less, by the procedure.

The cushioning adhesive sheet (1) may have a flexible substrate (6) fixed on the plane major surface (5) of the base part (10) on which no convex part is provided. The form in which the cushioning adhesive sheet (1) is adhered on the adherend surface (31) is useful as a cushioning structure which releases an impact force applied from the side of the plane major surface (5) of the base part (10) on which no convex part is provided before the impact force transfers to the adherend (3).

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In other words, the present invention provides an utilization form of the self-adhesive cushioning material in which the cushioning adhesive sheet (1) is used for adhering on the adherend surface (31). In this case, the flexible substrate (6) is useful to make the handling of the cushioning adhesive sheet (1) easy when the cushioning adhesive sheet (1) has a comparatively high flexibility and the plane major surface (5) on which no convex part is provided has adhesiveness.

As the flexible substrate (6), there can be used a polyester film, a polyvinyl chloride (and the polymer thereof) film, a polycarbonate film, a polyamide film, a polyolefin (and the copolymer thereof) film, an acrylic copolymer film etc. The thickness of the flexible substrate (6) is generally within a range of 10 to 200µm. In addition, an adhesion promoting treatment such as corona treatment, primer treatment, etc. can be carried out at the interface between the plane major surface (5) of the base part (10) on which the convex part is not provided and flexible substrate (6).

In addition, as shown in Fig. 3 (a), two cushioning adhesive sheets can be laminated to each other to form a cushioning material having a multi-layer structure. In this case, it has an airtight chamber (44) in the interior of the cushioning material, in addition to the airtight space (41). In this case, as shown in the penetrative top view of Fig. 3 (b), a provided wall (13) enclosing the airtight chamber (44) is preferably adhered on the base part (10) of the lower cushioning adhesive sheet at the position which generally corresponds to the center of the airtight space (41), in order to enhance the cushioning effect.

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As the adherend to be used for applying the cushioning adhesive sheet thereon, a material having smooth and flat surface having no void, which can form an effective airtight space at the time of applying this adhesive sheet may be employed. Examples of the material include glass, ceramic (china), plastic, metal, etc.

The cushioning adhesive sheet of the present invention is useful for a packing material for preventing the adherend from breaking during transferring, or the surface protective material for preventing the adherend surface from damaging, as the embodiment utilizing the excellent cushioning ability thereof. It is particularly suitable for protective applications such as window, top plate of desk, lens, dish, cup, vase, etc. Because the cushioning adhesive sheet of the present invention is superior in adhesiveness to glass and china, and the airtight space is easily formed and maintained thereon.

The cushioning adhesive sheet of the present invention may be used even when the peel strength from the adherend is very small (i.e. 180 degree peel strength is near zero), provided it has the retaining force of within a predetermined range. For example, when a plurality of glass plates are stacked and packed, a failure due to the contact between glass plates can be prevented by interposing the cushioning adhesive sheet between two glass plates. A high peel strength is not also necessarily when it is used as the surface protective material of the top plate of the glass plate disposed horizontally.

The retaining force in this case is measured as follows. Firstly, a cushioning adhesive sheet (1) having a size of 25 mm x 50 mm is placed on the surface of a green plate glass deposited vertically in the atmosphere (temperature: 25°C, humidity: 60 %RH) to adhere the whole adhesive surface (12) thereon. The time required for peeling off at any position of the adhesive surface (12) by the weight of itself is measured. The retaining force of the cushioning adhesive sheet of the present invention is preferably not less than 10 minutes, particularly not less than 600 minutes.

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# Process for Producing Cushioning Adhesive Sheet

In a preferred embodiment of the present invention, the cushioning adhesive sheet (1) is produced as follows.

A preliminary component comprising a monomer component containing isooctyl acrylate and acrylic acid in a predetermined proportion, and a photoinitiator component is charged in a stirring device, and is subjected to ultraviolet polymerization with stirring. At this stage, a partial polymerization is carried out so that the viscosity becomes a value within a range of 100 to 100,000 cps to prepare a partially polymerized syrup. To this syrup, a predetermined amount of a crosslinking agent monomer, 1,6-hexanediol diacrylate, and an additional photoinitiator are added, and the resultant is mixed uniformly to prepare a precursor composition of the cushioning adhesive sheet. The interior of the stirring device is generally purged with an inert gas such as nitrogen gas, etc. at the time of photopolymerization. Such a polymerization reaction generally does not include a heating step.

On the other hand, a mold having a predetermined geometric structure for molding a cushioning adhesive sheet is prepared as follows.

As is schematically shown in Fig. 4 (a), a positive mold (80) having a predetermined geometric structure of a comparatively hard plastic is prepared. As the plastic, there can be used acrylics, polycarbonates, etc. A detachable resin is brought into contact with this positive mold and those obtained by curing the detachable resin at normal temperature are detached from the positive mold (80) to form a negative mold (81). Examples of the positive mold include "Acrisunday plate (trade name)" manufactured by Acrisunday Co., Ltd. Examples of the peelable resin include templating silicone SE9555 manufactured by Toray Dow Corning Co., Ltd.

Then, as is schematically shown in Fig. 4 (b), a precursor composition (82) of the above cushioning adhesive sheet is brought into contact with the negative mold (81) and the composition (82) is covered with a transparent film. At this time, the negative mold (81) and film (83) are disposed at a predetermined distance so that the part (822) which will become a base part of the cushioning adhesive sheet and the part (821) which will become a convex part are formed, when the composition (82)

is polymerized and crosslinked (i.e. curing reaction). At this situation, ultraviolet ray is irradiated on the film (83) to complete the curing reaction and, after the negative mold (81) and film (83) are removed, a cushioning adhesive sheet of a cured article of the composition (82) is obtained.

The transparent film (83) is used for the purpose of barring oxygen and making flat the plane major surface (5) of the base part (10) on which the convex part is not provided. Such a transparent film (83) can also be used as the flexible substrate (6) fixed on the base part (10), as described above. As the film (83), a flexible plastic film such as polyester (PET) is generally used. In addition, the following method is used in order to determine the thickness of the base part.

That is, an excess amount of the precursor composition (82) is poured into the negative mold (81), the film (83) is covered thereon to form a precursor-containing laminate (8). Then, the laminate (8) is passed through a gap of a knife coater having the gap fixed in a predetermined distance, and the excess precursor composition (82) is discharged from the edge part to adjust the thickness and flatness of the part (822) which will become the base part.

As described above, when using ultraviolet ray as a polymerization energy, the wavelength of ultraviolet ray is generally 300 to 400 nm, and the irradiation intensity is within a range of 100 to 1,000 J/cm<sup>2</sup>.

The above positive mold can also be formed by carving a glass plate having a sufficient thickness using a sanding method. Furthermore, as the negative mold, there can be used a metal mold of which molding surface is treated with fluorine resin (e.g. Teflon<sup>TM</sup>).

#### 25 Other Additives

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The cushioning adhesive sheet (1) may contain various additives which are used in a normal pressure-sensitive adhesive unless the effect of the present invention is deteriorated. Examples of the additive include tackifiers, plasticizers, ultraviolet absorbers, antioxidants, polymerization initiators (e.g. those to be added at the production of adhesive polymer, such as photoinitiators, etc.), colorants, fillers, etc. These additives are included in the base part which is integrated with the convex part and/or the concave part, together with the adhesive polymer.

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#### Other Utilizations

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The cushioning adhesive sheet of the present invention forms an airtight space between the sheet and adherend, and maintains the airtight space even after applying. Therefore, it can also be utilized for forming a material selected from the group consisting of a vibration-deadening material, a soundproofing material and an insulating material, and an adhered composite material having a plurality of the functions. When the airtight space forms a decorative solid pattern, it can also be utilized for forming a material of a decorative sheet.

The convex part (11) may be coated with a flexible film, and the adhesive surface (12) may be adhered to the film, thereby, the airtight space may be enclosed as a cellular chamber from the beginning. In this case, the adhesive interface between the convex part of the cushioning adhesive sheet and flexible film is sealed, the convex part is crosslinked and has a suitable cohesive force (storage modulus controlled within a predetermined range and its decrease proportion), thereby, leaking of the air from the cellular chamber is prevented. Accordingly, the cellular chamber-enclosing sheet formed from the cushioning adhesive sheet of the present invention can maintain the effect for a long period of time.

The cushioning adhesive sheet of the present invention may be employed as a packing material. When a body to be packed (adherend) is a thin rectangular body such as a case of floppy disks, the body may be sandwiched between two sheets of the adhesive sheet having a size larger than the major surface of the body, and an adhesive surface of the adhesive sheet was adhered to the surface.

A blank part of the adhesive sheet, which was protruded around an edge of the body should not be adhered to a side surface of the body, but the upper blank part and the lower blank part should be adhered to each other to pack the body. The packing procedure is convenient, because additional adhesive means is not required for packing. An adhesive surface of the blank part may be deformed, thereby, adhesiveness of the blank part may be controlled.

When the packing is broke, one may peel the adhered blank part or may cut off the part.

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A pulp materials such as a paper may be provided on a plane surface of the adhesive sheet of the present invention as the support. When the body is packed by using the adhesive sheet having a paper support, a stamp or an address may be denoted on it, and the packed body was directly used as a parcel, etc.

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#### **TEST METHODS**

#### **Modulus**

In the following Examples, the modulus G of the convex part (11) is a storage modulus measured under the above described conditions, using a dynamic analyzer "Model No.: RDA II" manufactured by Rheometrix Co. Further, a sample holder used for the measurement was a parallel plate having a diameter of 7.9 mm.

## Decrease of log<sub>10</sub>G

A change (decrease) in  $\log_{10}G$  is a value calculated from a fluctuation based on G at 25°C, which was read from a viscoelastic spectrum obtained within a rage of 25 to 125°C.

#### **Shape Imparting Properties**

The sheet was applied to an adherend (a glass slide), and if an airtight space corresponding to the concave part of the cushioning adhesive sheet was not formed, the sheet was evaluated as "NG", and if an airtight space was formed, the sheet was evaluated as "OK".

#### **Shape Retention**

An airtight space immediately after applying on the adherend (a glass slide) and then stored for 5 months after applying were compared. The case that a change was scarcely observed was evaluated as "OK" and the case that an obvious change was observed was evaluated as "NG". This comparison was made using a photograph (20x magnification, taken through a glass slide) of the immediate sample and 5 months sample.

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#### Volume of Airtight Space

This is a value calculated from the volume of the concave part (4) of the cushioning adhesive sheet (1) before applying to the adherend. For example, when the concave part (4) has a shape lacking in one bottom surface (or side surface) of geometric solids such as truncated pyramid, rectangular parallelopipedon, etc., it can be calculated from its geometric size.

#### **Cushioning Ability**

The cushioning adhesive sheet was applied on one surface of a breakable test piece (glass slide) so as to cover almost all of the surface, and the resultant was employed as a sample. At this time, the applying pressure should be constant. In order to make the pressure constant, a press roller (2 kg) was used and the roller was once moved back and forth on the cushioning adhesive sheet placed on the test piece. The slide glass was a "MICRO SLIDE GLASS (trade name), No. 1" manufactured by Matustomi Glass Industries Co. Ltd. and had a size of 76 mm in length x 26 mm in width x 1 mm in thickness.

The sample made as described above was placed on a iron plate through a paper towel "FUJI PAPI (trade name)" manufactured by Taiyo Shigyo Co., Ltd., so that a surface of the sample, on which the cushioning adhesive sheet was applied, look upward, and an iron ball having a predetermined weight was dropped from a predetermined height. A test was started from the height of 30 cm using an iron ball having a diameter of 15 mm and a weight of 30 g. When the breakable test piece was not broken by dropping a ball from the height of 30 cm, a falling ball impact test was carried out according to the same manner as that described above except for changing the height to 40 cm. Thereafter, the height was increased by 10 cm until the test piece was broken and the height which was 10 cm smaller than the height where the breakage arose was taken as an evaluated value (cm) (test conditions: temperature; 25°C, humidity; 60%).

#### 30 Peel Strength

This is a value obtained by measuring the peel resistance, which was obtained by peeling off the cushioning adhesive sheet applied on the glass slide in

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the 180 degree direction at a stress rate of 300 mm/minute using a tensile testing machine, under the condition of an environmental temperature of 25°C and a humidity of 60% RH. Since the cushioning adhesive sheet of the present invention was adhered only by the adhesive surface of the convex part, the measured peel resistance shows maximum and minimum values. Accordingly, maximum and minimum values and an average value obtained by dividing the sum of them with 2 are shown as the measured results.

#### **EXAMPLES**

#### 10 Example 1

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A partially polymerized syrup was prepared by UV polymerizing a preliminary component comprising a monomer component of 90 parts by weight of isooctyl acrylate and 10 parts by weight of acrylic acid and 0.1 parts by weight of azobisisobutyronitrile (AIBN) as the photoinitiator. To this syrup, 1 part by weight of 1,6-hexanediol diacrylate as the crosslinking agent monomer and 0.2 parts by weight of AIBN as the additional photoinitiator were added and the result was uniformly mixed to prepare a precursor composition of a cushioning adhesive sheet.

A cushioning adhesive sheet was prepared by ultraviolet curing according to the method shown in Fig. 4, using "Acrisunday plate (trade name), Model No. Dia" manufactured by Acrisunday Co., Ltd. as the positive mold and "templating silicon, Model No. SE9555" manufactured by Toray Dow Corning Co., Ltd. as the peelable resin. As the transparent film, a PET film "Lumilar 50T (thickness, 50µm)" manufactured by Toray Co., Ltd. was used and, it was fixed to the base part after forming the cushioning adhesive sheet and utilized as the flexible substrate.

The shape of the concave part of the cushioning adhesive sheet was a truncated pyramid (width of adhesive surface side is wide) and its volume was 6 mm<sup>3</sup>. In addition, the width and length of the adhesive surface side of the convex part were 1 mm and 3 mm, respectively, and the thickness of the base part was 0.5 mm. Furthermore, the concave part was arranged in the proportion of 9/cm<sup>2</sup> (interior of horizontal surface, lattice pattern).

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Modulus, decrease of log<sub>10</sub>G within a range of 25 to 125°C, shape imparting properties, shape retention, cushioning ability and peel strength of the resulting cushioning adhesive sheet were evaluated. The results are shown in Table 1.

#### 5 Example 2 to 6

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According to the same manner as that described in Example 1 except for changing the amount of 1,6-hexanediol diacrylate as the crosslinking agent monomer as shown in Table 1, a cushioning adhesive sheet was obtained and evaluated. The results are shown in Tables 1 and 2.

In Examples 5 and 6, the 180 degree peel strength was nearly zero, but the sheet had enough tack to maintain the airtight space. Accordingly, the cushioning adhesive sheet did not shift from the position where the glass slide was adhered even if the sample was transported after applying.

In addition, the retaining force of the sheets of Examples 5 and 6 was measured by the above-described method. As a result, they were 10 minutes and 12 hours, respectively. Further, the retaining force of the sheets of Examples 1 and 4 showed not less than 48 hours (measurement was stopped within 48 hours).

#### Comparative Example 1

According to the same manner as that described in Example 1 except for using only isooctyl acrylate as the monomer component and using no crosslinking agent, a cushioning adhesive sheet was obtained and evaluated. The results are shown in Table 2.

#### 25 Comparative Example 2

According to the same manner as that described in Example 1 except for using no crosslinking agent, a cushioning adhesive sheet was obtained and evaluated. The results are shown in Table 2.

#### 30 <u>Examples 7 to 12</u>

According to the same manner as that described in Example 1 except for using as the positive mold those obtained by carving a glass having a thickness of

about 5 mm according to a sanding method and forming a concave-convex pattern so that the concave part of the cushioning adhesive sheet made from the mold becomes a rectangle having a predetermined size, a cushioning adhesive sheet was obtained and evaluated. The results are shown in Tables 2 and 3.

The size of the space of the concave part of the respective Examples is as follows.

Example 7: The top surface (bottom surface) is a square having a side of 1 mm and the height is 1 mm.

Example 8: The top surface (bottom surface) is a square having a side of 2 mm and the height is 1 mm.

Example 9: The top surface (bottom surface) is a square having a side of 3 mm and the height is 1 mm.

Example 10: The top surface (bottom surface) is a square having a side of 5 mm and the height is 1 mm.

Example 11: The top surface (bottom surface) is a square having a side of 10 mm and the height is 0.8 mm.

Example 12: The top surface (bottom surface) is a square having a side of 10 mm and the height is 1.5 mm.

In all Examples, the width of the convex part was 1 mm and the thickness of the base part was 0.2 mm.

#### Example 13

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According to substantially the same manner as that described in Example 1, a cushioning adhesive sheet (containing no flexible substrate) having a concave part of which top surface (bottom surface) is a square having a side of 3 mm (height: 0.5 mm) and a base part having a thickness of 0.5 mm and that obtained by fixing a PET film (flexible substrate) to the base part of the same cushioning adhesive sheet were separately prepared and they were laminated to each other by a self adhesive force to obtain a composite cushioning adhesive sheet. According to the same manner as that described in Example 1, the composite was evaluated. The results are shown in Table 3.

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#### Comparative Example 3

According to the same manner as that described in Example 1 except for molding into a flat sheet (no concave-convex part) having a thickness of 1.2 mm, an adhesive sheet was obtained and evaluated. The cushioning ability was 30 cm, and the 180 degree peel strength was 1150 g/25 mm.

#### Comparative Example 4

According to the same manner as that described in Example 1 except for using a prism film "SOLF (trade name)" manufactured by 3M Co., as the positive mold, a cushioning adhesive sheet was obtained and evaluated.

"SOLF" has a structure comprising a plurality of prism projections in which a plurality of trigonal prisms having an isosceles triangle (height: about 0.18 mm, base: about 0.36 mm) as the bottom surface are horizontally disposed in parallel with each other. The space of the concave part between adjacent prisms is composed of the same trigonal prism as that described above. Accordingly, the cushioning adhesive sheet can form only a space having an opening on the bottom surface side of the trigonal prism (no airtightness).

The cushioning ability was 30 cm, and the 180 degree peel strength was 50 g/25 mm.

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#### Example 14

The cushioning adhesive sheet of Example 1 was formed so that it has an area of 8 cm x 10 cm. The sheet was applied on the above PET film "Lumilar 50T" manufactured by Toray Co., Ltd. so that the convex part side faced to the PET film to prepare a cellular chamber enclosing sheet. This sheet was placed on a flat laboratory-table and allowed to stand under the condition of an environmental temperature of 25°C and a relative humidity of 60% RH for 7 days at the state where a static load (4 kg/8 cm x 10 cm) is applied thereon to evaluate the maintaining performance of the cellular chamber to the static load.

The sheet was evaluated according to the same manner as the above shape retention. As a result, the cellular chamber was scarcely deformed.

The same test was carried out using "Air bag (trade name), Model No. #37" manufactured by Kawakami Sangyo Co., Ltd. as a control sample. This air bag is molded from a non-adhesive thermoplastic film (considered to be a polyolefin film) and is a cushion sheet enclosing many cellular chambers, each of which has a height of about 3 mm and a volume of about 230 mm<sup>3</sup>.

After 7 days, almost all of air leaked from the air chamber.

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In addition, the cushioning ability of this air bag was evaluated according to the same manner as that described above. As a result, it was 40 cm. When four air bags were stacked and was disposed on the glass slide, the evaluation value of 80 cm was obtained.

Table 1

			Taule	<u> </u>		
		Ex. 1	Ex. 2	Ex. 3	Ex. 4	Ex. 5
Crossii agent (	_	1.00	0.25	0.50	2.00	5.00
Moduli (dynes/		6.7 x 10 <sup>3</sup>	6.0 x 10 <sup>3</sup>	6.0 x 10°	1.1 x 10°	2.0 x 10°
∆log <sub>10</sub> (	3	0	-0.4	-0.2	+0.1	+0.2
	e of air- ace (mm³)	6	6	6	6	6
Shape i	mpart	OK	OK	ОК	OK	ОК
	etention	OK	OK	OK	OK	ОК
Cushio	ning (cm)	80	60	70	70	60
Peel streng th (g/25 mm)	Max. Avg. Min.	450 350 250	1600 1000 400	1000 675 350	65 50 35	~0

Table 2

		Ex. 6	C. Ex. 1	C. Ex. 2	Ex. 7	Ex. 8
Crosslinkin (p.b.w)	ig agent	10.00	0	0	1.00	1.00
Modulus G (dynes/cm²		4.0 x 10°	3.8 x 10 <sup>3</sup>	5.8 x 10 <sup>3</sup>	6.7 x 10 <sup>3</sup>	6.7 x 10 <sup>3</sup>
∆log <sub>10</sub> G		+0.2	-2	-2	0	0
Volume of space (mm		6	6	6	1	4
Shape impa	urt	ОК	NG	OK	OK	OK
Share reten	tion	OK	NG	NG	OK	OK
Cushioning	(cm)	60		-	90	80
Peel strength (g/25mm)	Max. Avg. Min.	~0	-	•	1400 1100 800	1350 875 400

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Table 3

		Ex. 9	Ex. 10	Ex. 11	Ex. 12	Ex. 13
Crosslinking (p.b.w)	g agent	1.00	1.00	1.00	1.00	1.00
Modulus G (dynes/cm²)		6.7 x10 <sup>3</sup>	6.7 x 10 <sup>3</sup>			
Δlog <sub>10</sub> G		0	0	0	0	0
Volume of a space (mm <sup>3</sup>	•	9	25	80	150	4.5x2
Shape impart		OK	OK	OK	OK	OK
Share retent		OK	OK	OK	OK	OK
Cushioning	(cm)	90	50	50	50	110
Peel	Max.	00	880	650	650	1000
strength	Avg.	50	490	280	275	650
(g/25mm)	Min.	00	100	90	80	300

#### Examples 15 to 17

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A cushioning adhesive sheet was prepared as the same manner as described in Example 9, except that the flexible support (a PET film) was not provided and a volume of the concave part is controlled as shown in Table 4. The vibration-deadening ability of the cushioning adhesive sheet was evaluated by using a vibration analyzer manufactured by Hewlett-Packard Co. "3562A Dynamic Signal Analyzer", as follows.

An adhesive surface of the convex part of the adhesive sheet was adhered on the whole surface of the first metal sheet (an aluminum sheet) having a size of 25 mm (width) x 100 mm (length) x 2 mm (thickness) to form airtight spaces. A detector manufactured by PCB (PIZETRONICS) Co., "Acceleration Pick Up" was set on about center of a surface of the first metal sheet. Substantially the same metal sheet was then adhered on the another main surface of the adhesive sheet to prepare the sample.

A surface of the second metal sheet was pounded once by using a metal bar having a diameter of 3.5 mm and a decaying constant (h) is calculated by analyzing a vibration detected on the first metal sheet. The measurement was carried out three times and average thereof was adopted as an evaluation for vibration-deadening ability.

The decaying constant (h) is defined by the following equation.

 $h = X_1/X_2$  wherein,  $X_1$ , represents the first amplitude, and  $X_2$  represents the second amplitude.

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When the decaying constant is more than 1 and becomes a large value, it represents excellent vibration-deadening ability. The results are shown in Table 4.

#### Comparative Example 5

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A sample was prepared and the decaying constant (h) thereof was determined according to the same manner as described in Example 15, except that a plane adhesive sheet having no convex part was used. The results are shown in Table 4.

Table 4

	Volume of Concave Part (mm3)	Decaying Constant (h)
Ex. 15	3x3x3=9	2.0
Ex. 16	5x5x1=25	2.1
Ex. 17	10x10x1=100	2.3
C. Ex. 5	0	1.7

It has been known to the art that a sheet of acrylic adhesive sheet as described 10 in Comparative Example 5 has good vibration-deadening ability (For example, see Japanese Laid-Open Utility Model Publication No. 4-126369). But cushioning adhesive sheets of Examples 15--to 17 exhibit the decaying constant grater than Comparative Example 5.

According to the present invention, there is provided a cushioning adhesive sheet which can maintain a plurality of independent airtight spaces having a comparatively large volume, stably, with time even after the completion of application. By applying such a cushioning adhesive sheet on an adherend, there can be formed an adhesive structure which is superior in effect of releasing an impact

20 force transmitted to the adherend.

#### - 30 -

#### **CLAIMS**

What is claimed is:

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- 1. A cushioning adhesive sheet comprising:
- (i) a base part; and
- (ii) a convex part comprising a crosslinked adhesive polymer and having an adhesive surface which is provided on at least one major surface of the base part so as to enclose a plurality of concave parts having a geometric shape;

wherein a volume of the concave part is 0.8 to 600 mm<sup>3</sup>, a modulus G of the convex part measured according to a dynamic viscoelasticity measuring method at a frequency of 1 rad/second under shear mode at 25°C is within a range of 5 x  $10^5$  to 4 x  $10^6$  dynes/cm<sup>2</sup>, and a decrease of  $\log_{10}$ G within a range of 25 to 125°C is less than 1.0.

- 2. The cushioning adhesive sheet according to claim 1, wherein the base part comprises a crosslinked adhesive polymer and has a structure integrated with the convex part.
  - 3. The cushioning adhesive sheet according to claim 1, further comprising a layer of a flexible substrate on a plane major surface of the base part on which the convex part is not provided.
  - 4. The cushioning adhesive sheet according to claim 1, wherein the crosslinked adhesive polymer is prepared by polymerizing a monomer component containing alkyl (meth)acrylate, ethylenically unsaturated acid, and 0.5 to 5% by weight of a crosslinking agent monomer having two or more (meth)acryl groups in the molecule.
  - 5. A cushioning structure comprising an adherend and the cushioning adhesive sheet of claim 1 adhered on an adherend surface, said cushioning structure comprising an airtight space consisting of an adherend surface and an inner surface of the concave part.

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6. The cushioning structure according to claim 5, wherein a peel strength measured at 25°C when the cushioning adhesive sheet is peeled off from the adherend surface is within a range of 20 to 2,500 g/25 mm.

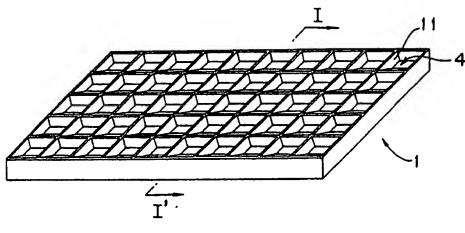
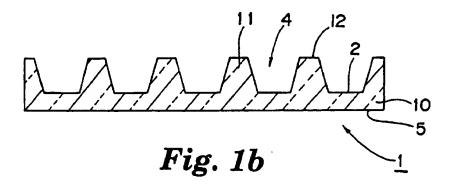
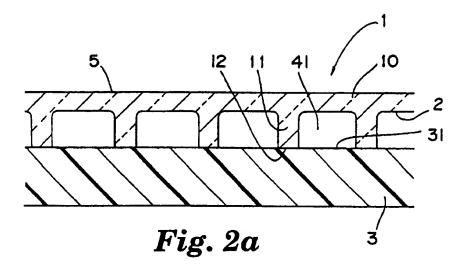
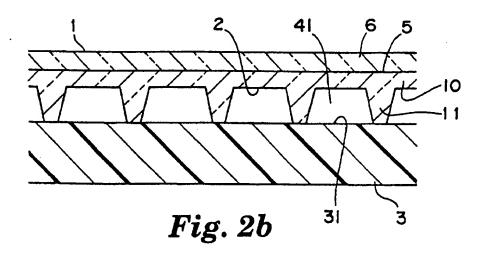
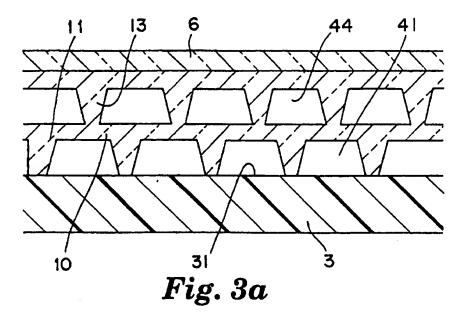


Fig. 1a









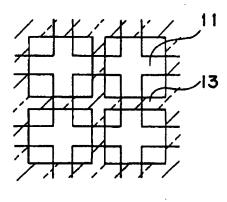
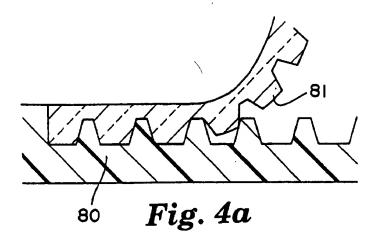


Fig. 3b



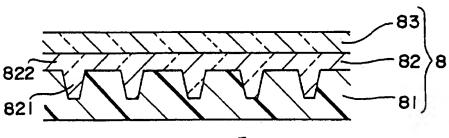
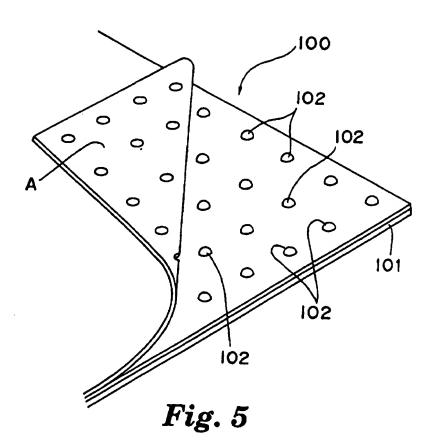
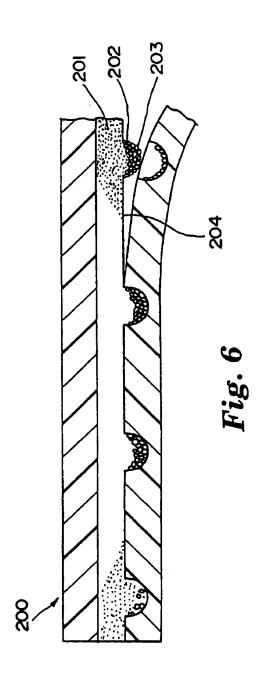
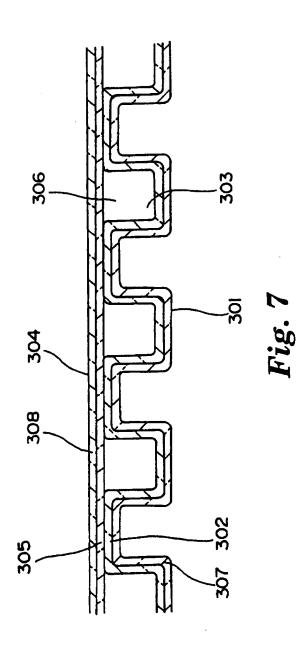


Fig. 4b





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13 March 1996 (13.03.96)

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(74) Agents: SKOLNICK, Steven, E. et al.; Minnesota Mining and Manufacturing Company, Office of Intellectual Property Counsel, P.O. Box 33427, Saint Paul, MN 55133-3427 (US).

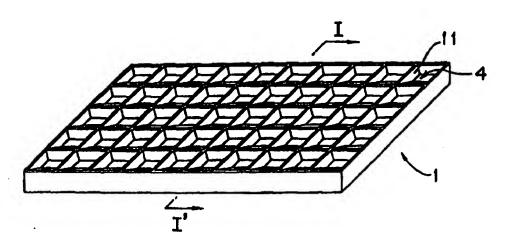
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#### (57) Abstract

A cushioning adhesive sheet for which the cushioning ability is not likely to be deteriorated with time, by applying an airtight space having a comparatively large volume on an adherend and maintaining the airtight space stably with time. The cushioning adhesive sheet comprises: i) a base part; and ii) a convex part consisting of a crosslinked adhesive polymer and having an adhesive surface, which is provided on at least one major surface of the base part so as to enclose a plurality of concave parts having a geometric shape; wherein a volume of the concave part is 0.8 to 600 mm<sup>3</sup>, a modulus G of the convex part measured according to a dynamic viscoelasticity measuring method at a frequency of 1 rad/second under shear mode at 25 °C is within a range of 5 x 105 to 4 x 106 dynes/cm2, and a decrease of log10G within a range of 25 to 125 °C is less than 1.0.

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information on patent family members

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Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 5344681 A	06-09-94	CA 2115673 A EP 0603208 A JP 6510554 T WO 9305123 A US 5449540 A	18-03-93 29-06-94 24-11-94 18-03-93 12-09-95
EP 0266094 A	04-05-88	US 4786537 A AU 592894 B AU 7892487 A CA 1275009 A DE 3775170 A HK 55092 A JP 2505224 B JP 63121041 A	22-11-88 25-01-90 05-05-88 09-10-90 23-01-92 30-07-92 05-06-96 25-05-88